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RESEARCH ARTICLE

Coapplication of water treatment residual and compost for increased phosphorus availability in arable sandy soils

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Abstract

Introduction: Soil degradation coupled with poor access to organic nutrient resources remains a major constraint in increased crop productivity in sub-Saharan Africa, thus hindering the continent's efforts in achieving the United Nations' Sustainable Development Goals, particularly goals 1 (end poverty), 2 (zero hunger) and 3 (improve human health). Water treatment residual (WTR), a by-product of clean water treatment, has been identified as an alternative organic nutrient resource for crop production. However, there are some inconsistences in soil phosphorus (P) dynamics following aluminium WTR (AI-WTR) application.

Materials & Methods: A laboratory experiment was conducted to evaluate the P sorption of a sandy soil amended with 10% Al-WTR, 10% compost (C) as a quasicontrol, 10% C + 10% Al-WTR (10% coamendment) and 5% C + 5% Al-WTR (5% coamendment) under varying levels of pH, particle size and P concentration. We calculated crop P fertilizer requirements under different amendments.

Results: The results demonstrated that all amendments exceeded the minimum of 0.2 mg P L⁻¹ needed in soil solution at equilibrium to maintain plant growth. However, the maximum P sorption capacity was higher for 10% Al-WTR single amendment, ranging from 770 to 1000 mg P Kg⁻¹, and from 714 to 1000 mg P Kg⁻¹ and 555 to 909 mg P Kg⁻¹ for 10% and 5% coamendments, respectively, across a range of pH and soil particle size fractions. The coamendments showed a reduction in crop P fertilizer requirements by ranges of 30–60% and 60–70% for the 10% and 5% coamendment levels, respectively, across different pH and particle sizes, relative to 10% Al-WTR.

Conclusion: Results show that the use of 5% coamendment in sandy soils increases P availability sufficiently to improve crop yields. The results provide scope for using AI-WTR coamendments to rebuild soil health in sandy soils in urban agriculture and increase macronutrient provision in crops to support human health.

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KEYWORDS

aluminium water treatment residual, coamendment, increased crop productivity, phosphorus fertilizer requirement, soil health

1 | INTRODUCTION

Soil degradation and poor soil health remain major challenges for attaining food and nutrition security in sub-Saharan Africa (SSA), diminishing prospects for achieving the United Nations' Sustainable Development Goals (SDGs) numbers 1, 2 and 3 that aim to end poverty, hunger and improve human health, respectively. This has largely been attributed to the long-term mining of soil nutrients through harvested products with no or minimal use of fertilizers as well as limited retention of crop residues (Mtangadura et al., 2017; Obalum, 2017). African smallholder farmers rely mainly on locally available organic nutrient resources, for example, manure and woodland litter, to replenish soil fertility for sustainable crop production (Mapfumo & Giller, 2001). However, the organic nutrient resources traditionally used by smallholder farmers have become scarce due to the deterioration of livestock heads (Herrero et al., 2014) and woodlands (Chagumaira et al., 2016), prompting the need to explore alternative organic nutrient resources. Organic nutrient resources are a springboard for improved soil health and especially in the rehabilitation of degraded soils (Zingore et al., 2005), which occupy about 30% of arable land in Africa (Kihara et al., 2020; Nezomba et al., 2015). Aluminium water treatment residual (Al-WTR). a by-product of potable water treatment, has been identified as a potential organomineral soil nutrient resource for sustainable crop productivity in urban agriculture (Kerr et al., 2022). Urban agriculture has increasingly been embraced by African governments for increased food and nutrition security in cities (Dassanayake et al., 2015; Nkrumah, 2019; Turner et al., 2019).

Al-WTRs can potentially build soil organic carbon in the long term due to their high carbon content, which ranges from 12.7% to 26% as reported by Dassanayake et al. (2015) and Kerr et al. (2022). When AI-WTR is added to the soil, iron (Fe) and aluminium (AI) oxide mineral surfaces within the WTR potentially form strong bonds with soil organic matter (SOM) (Yan et al., 2016), thus protecting SOM from microbial decomposition (Kögel-Knabner et al., 2008). The use of Al-WTR as a coamendment has been associated with increased soil aeration, aggregation and water retention (Hsu & Hseu, 2011; Kerr et al., 2022), and increased crop yield and plant micronutrients such as zinc and copper (Gwandu et al., 2021; Mahmood-ul-Hassan et al., 1993). On the other hand, the use of AI-WTRs in agriculture serves as an important alternative disposal route to landfill (Turner et al., 2019). This saves urban authorities/councils millions of dollars that would have been used for disposal of AI-WTR, as its production is projected to drastically increase in African urban cities, with an increase in demand for potable water (Saghir & Santoro, 2018). The projected increase in the production of Al-WTR creates opportunities for its reuse as a resource. Water treatment works are also looking for sustainable ways of reusing their WTR, aligning with SDG12, which relates to responsible production and consumption.

Even though research has demonstrated the usefulness of Al-WTR as a soil amendment (e.g., Clarke et al., 2019; Gwandu et al., 2021; Kerr et al., 2022), there are still concerns about the interaction of Al-WTR and soil phosphorus (P) (Lombi et al., 2010; Silveira et al., 2013), one of the most limiting nutrients for crop production in Africa (Rurinda et al., 2020). Increased soil P available for plant uptake enhances plant root development, which boosts their capacity to take up nutrients from the soil, thus improving overall crop productivity (Malhotra et al., 2018). Many studies have shown a decrease in plant-available P when AI-WTR is used as a single amendment (e.g., Mahmood-ul-Hassan et al., 1993; Penn & Camberato, 2019). This has been attributed to P sorption by the amorphous AI and Fe present in the AI-WTR (Brennan et al., 2019; Silveira et al., 2013). It is suggested that P becomes fixed to Al-OH groups due to their high zero potential charge, rendering P unavailable for plant uptake (Babatunde et al., 2008; Bai et al., 2014). While this characteristic could be important in retaining excess P (Novak & Watts, 2004; O'Connor et al., 2002), it is a major drawback where soil P is in limited supply as in Africa. Most arable soils in Africa, many of which are sandy, require the continual application of P to sustain crop production.

The use of AI-WTR in combination with other organic nutrient sources such as compost or manure may reduce P sorption associated with Al-WTR (Lin et al., 2017; Yang et al., 2019). Humidified substances produced during the decomposition of organic materials enhance the bioavailability of P in acidic soils since they have a greater affinity for Al oxides compared to phosphates (Quan-Xian et al., 2008). Coapplication of Al-WTR and P fertilizer has been suggested as a possible route for the alleviation of P limitations in Al-WTR amended soils (Hyde & Morris, 2004; Mahmood-ul-Hassan et al., 1993), but the major challenge is that African smallholder farmers have limited access to P mineral fertilizers. Previous results from a greenhouse experiment with maize (Zea mays L.) as a test crop showed that the addition of P fertilizer at a constant rate of 14 kg P ha⁻¹ to 10% or 20% AI-WTR amendment levels was not enough to offset the P sorption associated with Al-WTR (Gwandu et al., 2021). Gwandu et al. (2021) showed that the maize P content was $<3 g kg^{-1}$, which is the critical limit for P accumulation in maize plant tissue (Tandon, 1993).

P sorption refers to processes that result in the removal of P from soil solution mainly by surface adsorption and precipitation reactions (Arias et al., 2006). Sorption of applied P results in reduced plant available P, thus reducing plant productivity (Vitousek et al., 2010). P sorption is dependent upon biogeochemical and environmental factors such as pH, soil texture, soil composition (clay type, organic matter, Al and Fe oxides), soil management practices and fertilizer sources (Fink et al., 2016, 2016; Gérard, 2016). For example, the movement of P is limited in soils with high clay content due to

sorption by soil colloids (Börling et al., 2001; He et al., 1999), while P leaching and transportation are greater in sandy soils. Soil particle size also plays an important role in P retention in soils (Atalay, 2001). In high pH soils, P retention and transportation are dependent on surface adsorption and precipitation, while in acid soils, P is fixed into insoluble forms by sorption reactions with Fe and Al oxides (Börling et al., 2001; Gérard, 2016), which are abundant in Al-WTR.

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While emerging evidence proved that AI-WTR and compost can be coapplied and used as a source of crop nutrients (Clarke et al., 2019; Gwandu et al., 2021), their combined use remains largely unexploited and has not been optimized. As such, information on their P sorption characteristics when coapplied as a soil amendment to sandy soils is scarce. This paper explores P availability and P sorption characteristics in a sandy soil amended with coamendments of AI-WTR and compost and quantifies the crop P fertilizer requirements (PFRs) under different pH and soil particle sizes. The specific objectives were to (i) determine the effects of AI-WTR, and compost amendments on soil P sorption; (ii) determine the influence of particle size of amendments and soil solution pH on P sorption; and (iii) estimate crop P nutrient requirements under different soil amendments.

2 | MATERIALS AND METHODS

2.1 | Experimental site and Al-WTR and compost soil amendments

The sandy topsoil was sampled to a depth of 30 cm from a farm outside, Kuilsrivier, South Africa. The sandy parent material, in which the soils have formed results from aeolian processes and consist of well-sorted fine sand (Schloms et al., 1983; Steytler, 2020). These soils are typified by very low pH (pH 4.2) and low nutrient content (N, P, Ca, Mg and K) (Table 1). The low nutrient content is consistent with most sandy soils used for crop production in SSA (Chukwuka 2009; Mtambanengwe & Mapfumo, 2005). Soil macro- and micronutrient limitations have often been linked to low crop yields and malnutrition in smallholder farming systems in SSA (Kihara et al., 2020; Mtangadura et al., 2017). The sandy soil was sampled to a depth of 30 cm, air-dried and sieved to 2 mm. It was stored at room temperature before being characterized for physical and chemical properties (Table 1). The compost used was a commercial grade, Prime Pure organic compost, sourced from a local hardware store in Stellenbosch, South Africa and three subsamples were characterized for chemical properties as shown in Table 1.

WTR was sampled from a landfill stockpile at Prince Edward Water Treatment Plant (WTP) ($17^{\circ}58'45''$ S; $31^{\circ}4'11''$ E), which is located 22 km to the Southwest of Harare, the capital of Zimbabwe. The WTP uses the conventional water treatment system consisting of sludge blanket clarifiers and rapid sand filters. Aluminium sulphate (Al₂(SO4)₃·14H₂O) is used as a flocculant. Sulphuric acid, chlorine gas, ammonia, flocculated carbon and lime are used to optimize the water

TABLE 1 Physical and chemical characteristics of sand, compostand Al-WTR used in the experiment.

Parameter	Soil	AI-WTR	Compost	
Sand (%)	99.76ª	ND	ND	
Silt and clay (%)	0.24 ^a	ND	ND	
pH (0.01 M CaCl ₂)	4.23 ^d	6.93 ± 0.01	7.73 ± 0.00	
EC (μ S cm ⁻¹)	10.00	870 ± 0.03	5630 ± 0.05	
Total P (%)	0.005 ^a	0.12 ± 0.05	0.18 ± 0.03	
Available P (mg kg ^{-1})	2.43 ^a	7.6 ± 0.06	139.3 ± 0.05	
Total N (%)	0.03 ^a	0.74 ± 0.01	1.08 ± 0.01	
Total C (%)	0.60 ^a	18.90 ± 0.05	19.59 ± 0.01	
C/N ratio	15.00 ^a	25.50 ± 0.10	18.13 ± 0.01	
Ca (cmol _c kg ⁻¹)	0.55ª	3.40 ± 0.003	46.28 ± 0.003	
Mg (cmol _c kg ⁻¹)	0.264 ^a	0.58 ± 0.001	7.25 ± 0.005	
K (cmol _c kg ⁻¹)	<0.001ª	0.24 ± 0.002	21.00 ± 0.01	
AI (cmol _c kg ^{-1})	ND	5.61 ± 0.05	0.37 ± 0.07	
Dry matter (g) @ 105°C	98.60 (±0.02)	96.80 ± 0.03	41.50 ± 0.09	

Note: Data are means \pm standard error of the means (*N* = 3), except for soil where displayed data are means only.

Abbreviations: Al-WTR, aluminium water treatment residual; ND, not determined.

^aData are obtained from Steytler (2020).

^bDetermined using 1 M KCl.

treatment process (Engineer C. Chinyanya, personal communication, March 23, 2020). After sampling, the WTR was air-dried for 30 days. Three subsamples were characterized for physical and chemical properties as shown in Table 1. The Zimbabwean Al-WTR was used because it represents the WTR generated from most WTPs in SSA, which use aluminium sulphate as the flocculant.

2.2 | Presorption incubation procedure

Compost and Al-WTR were ground to pass through three different sets of sieves to obtain particle sizes of 2, 0.5 and 0.25 mm before mixing with the sandy soil. The soil was then mixed with compost or Al-WTR or their combination, culminating in four treatments consisting of (i) 10% Al-WTR, (ii) 10% compost, (iii) 10% compost + 10% Al-WTR (10% coamendment) and (iv) 5% compost + 5% Al-WTR (5% coamendment). A sample of 100 g from each amendment (dry matter basis) was placed into plastic containers and incubated at 25°C for 30 days. Deionized water was then added to each sample to field capacity, and this was maintained for the entire incubation period through weekly weight adjustments (Mafongoya et al., 2000). The container surfaces were covered using porous plastic films to maintain aerobic conditions.

2.3 **Experimental design**

The laboratory P adsorption experiment comprised of 4 soil amendments × 5 P concentrations × 3 soil pH levels × 3 amendments particle sizes arranged in a split-split plot design with three replications of each combination. Factorial combinations of treatments (four levels) were considered as whole plot, P concentration (five levels) as blocks, while particle size (three levels) and pH (three levels) were considered as sub-plot and sub-sub-plot, respectively. Particle size, pH and P concentration were purposefully defined in the experimental design and were thus considered as fixed factors.

2.4 P extraction and analysis (adsorption test)

From each incubated sample (5% coamendment, 10% coamendment, 10% C and 10% Al-WTR), 1 g was weighed into 50 mL centrifuge tubes. A range of different P concentrations (0, 10, 50, 100 and 200 ppm P) was set up, containing 0.01 M CaCl₂ to serve as a supporting electrolyte. The 0 ppm P was included in the experiment to take into account the release of P from the lyses of microbes. A 20 mL aliquot of each P concentration was added to a sample of each treatment. The pH was adjusted for each sample by adding predetermined amounts of either 0.01 M H₂SO₄ or 0.1 M NaOH. Chloroform (three drops per sample) was added to the mixture to inhibit microbial activity. The samples were shaken for 24 h at 200 rpm at 25°C, to facilitate absorption. After centrifugation (4500 rpm for 10 min) samples were filtered using 0.45-µm Millipore filter paper. The supernatant P concentration was determined colorimetrically with the ammonium molybdate-ascorbic acid method (Murphy & Riley, 1962) using a UV-Vis Jenway 6300 spectrophotometer at 880 nm. The pH and electrical conductivity of the different materials were measured with 0.01 M CaCl₂ (Anderson & Ingram, 1993) and readings were taken using standard meters for pH (Metrohm 827) and electrical conductivity (Jenway 4510). Total organic carbon was determined using the wet oxidation method (Anderson & Ingram, 1993). The samples were oxidized using a combination of potassium dichromate (K₂Cr₂O₇) and sulphuric acid (H_2SO_4) . The mixture was titrated using ferrous ammonium sulphate. The difference between added and residual $K_2Cr_2O_7$ gives a measure of organic C content in the sample (Okalebo et al., 2002).

2.5 Determination of sorption parameters

The Langmuir and Freundlich isotherms were used to understand the relationship between the quantity of P adsorbed per unit soil weight and the concentration of P in the solution. The Langmuir and Freundlich isotherms have often been used to describe P sorption characteristics (e.g., Jeppu & Clement, 2012; Olsen & Watanabe, 1957; Saeed et al., 2021). P adsorption parameters were calculated with the Langmuir isotherm equation

$$C_{\rm e}/Q = 1/bQ_0 + C_{\rm e}/Q_0,$$
 (1)

where Q is the mass of P adsorbed per unit mass of coamendment (mg kg^{-1}), C_{\rm e} the equilibrium concentration of P (mg P $L^{-1})$ in suspension after 24-h equilibrium, Q₀ the maximum adsorption capacity (mg $P kg^{-1}$) and b a constant related to the binding strength of P at the adsorption sites (L mg^{-1} P). A linear regression analysis was performed between C_e and C_e/Q , and the values for b and Q_0 were obtained from the slope and intercept of the regression line, respectively. $Q_0 \times b$ is the maximum adsorption buffering capacity (MBC, L kg⁻¹). The Freundlich equation is

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$$Q = kC_e^{b}, (2)$$

where Q is the mass of P adsorbed per unit mass of coamendment (mg kg⁻¹), C_e the equilibrium concentration of P (mg PL⁻¹) in suspension after 24-h equilibrium, k the proportionality constant for Freundlich equation (mg kg⁻¹) and b (b < 1) the slope of the curve $\log Q$ versus $\log C_e/Q$. The external P fertilizer requirement (PFR) was calculated based on the assumption that soil should contain 0.2 mg P L^{-1} in solution for optimum plant growth (Fox & Kamprath, 1970; Roy & De Datta, 1985). The P₂O₅ fertilizer requirement was calculated based on the method by Saeed et al. (2021). Briefly, the method takes into account the targeted P concentration in the equilibrium solution, the MBC and the P bonding energy constant (see Saeed et al., 2021).

2.6 Data analysis

The analysis of variance for a split-split plot design was used to analyse the effect of AI-WTR and compost amendments (treatments), pH, particle size and P concentration, as well as their interaction on P adsorption using GENSTAT 21st Edition (VSN International, 2022). Fischer's least significant difference was used to separate significant treatment means at p < 0.05.

| RESULTS AND DISCUSSION 3

3.1 Effect of different soil amendments on equilibrium P

The P sorption isotherms presented in Figure 1, generally show that equilibrium P in solution among the different soil amendments increased with an increase in P concentration. The equilibrium P in the solution increased exponentially with an increase in initial P concentration from 50 to 200 mg L^{-1} P (Figure 1). The concentration of P in solution at any given point followed the trend 10% C > 5% coamendment > 10% coamendment > 10% AI-WTR (Figure 1). However, the equilibrium P in solution varied mainly with particle size and was higher for particle size of 0.5 mm than for particle sizes of 0.25 and 2 mm across pH levels. The P in solution was generally similar for



FIGURE 1 Equilibrium phosphorus (P) concentration of a sandy soil amended with aluminium water treatment residual (AI-WTR) and compost or their combination at different pH and particle size. Error bars are the least significant differences (LSDs) of the treatment means (LSD) (*p* < 0.05). AI-WTR, aluminium water treatment residual; C, compost; p.s, particle size.

0.25-mm particle size. Atalay (2001) demonstrated a decrease in equilibrium P with a decrease in soil particle size, although this was more apparent in soils with high organic matter content. At 2-mm particle size, the effects of treatment on equilibrium P in solution were more apparent until 100 mg P L^{-1} , and beyond this concentration, the treatments were similar. It is apparent from the results that the coamendment of Al-WTR and compost resulted in an increase in equilibrium P concentration, relative to sole Al-WTR, but a decrease relative to sole compost. These results attest to the likelihood that organic matter reduced the P binding effects associated with Al-WTR, resulting in more P in thhe equilibrium solution.

3.2 | Effect of different soil amendments on P sorption

Apart from 10% C, which increased steadily throughout, P sorption across amendments (including the 0.25-mm particle size of 10% C) increased exponentially with an increase in P concentration until 50 mg L^{-1} P; thereafter, a slow increase was observed between 100 and 200 mg L⁻¹ P (Figure 2). The general trend shows that the amount of P sorbed at any given P concentration decreased in the order 10% Al-WTR > 10% coamendment > 5% coamendment > 10% C (Figure 2). For example, the highest P sorption (995.15 ± 2.40 mg P kg⁻¹) was recorded for 10% Al-WTR at a pH of 4.5 and a particle

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FIGURE 2 Phosphorus adsorption curves of a sandy soil amended with aluminium-water treatment residual (AI-WTR) and compost or their combination at different pH and particle size. Error bars denote the least significant differences (LSDs) of the treatment means at p < 0.001 (N = 3). AI-WTR, aluminium water treatment residual; C, compost; p.s, particle size.

size of 0.25 mm when 200 ppm P was added into the soil solution. This translates to 21.7%, 10.5% and 4.9% higher than 10% C, 5% coamendment and 10% coamendment, which attained 817.61 ± 5.96 , 900.85 ± 8.94 and $948.25 \pm 2.98 \text{ mg P kg}^{-1}$, respectively, under similar conditions (Figure 2). The lowest P sorption $(158.87 \pm 0.62 \text{ mg P kg}^{-1})$ by 10% Al-WTR was recorded at pH 7.5 for the 2-mm fraction after the addition of 10 ppm P, equating to 187.8%, 37.3% and 6.7% more adsorbed P relative to 10% C, 5% coamendment and 10% coamendment, in that respective order (Figure 2). The high P sorption capacity by 10% Al-WTR could be likely attributed to a higher amount of Al oxides present in the 10% Al-WTR amendment compared to the other amendments. Some studies have suggested that AI bound by organic complexes makes a large contribution to P sorption in soils (Bai et al., 2014; Gérard, 2016). Others suggest that P becomes fixed to Al-OH groups on the surface of the WTR and gets adsorbed via a precipitation reaction (Babatunde et al., 2008; Bai et al., 2014; Wang et al., 2012).

The 10% C amendment consistently exhibited very low P sorption compared to the rest of the amendments. Anions such as phosphate are not normally sorbed on organic matter (OM) due to repulsion by the negatively charged hydroxyl (-OH) and carboxyl (-COOH) ions in OM. The hydroxyl and carboxyl ions are instead preferentially sorbed over the phosphate by surface-bound Al and Fe oxides in most soils (Caporale et al., 2013; Wang et al., 2007). The coamendment of AI-WTR and compost resulted in a marked decrease in P sorption compared to sole Al-WTR (Figure 2). However, this was dependent on the AI-WTR-compost ratio, with a 5% level resulting in less P adsorption compared to 10% coamendment. From these results, it is apparent that the addition of compost to AI-WTR greatly contributed to an increase in P availability in the soil solution. This could be attributed to the direct release of P in the soil solution by the compost or alternatively, to the presence of OM from the compost. One mechanism suggested could be that the OM forms complexes with surface-bound Al or Fe to form soluble organic-metal

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compounds causing the release of the previously adsorbed P (Yan et al., 2016). Alternatively, OM may be adsorbed to soil particles at nonspecific sorption sites, increasing negative charges on the soil surface, thus repealing phosphate ions (Erich et al., 2002). Other reports suggest that decomposition products of organic matter (humified substances) compete for sorption sites with P and thus result in lower P sorption (Lin et al., 2017; Ohno & Erich, 1997; Yang et al., 2019). However, this was not the case for the 0.25-mm particle size under the 10% C amendment-in fact, the P sorption was higher than the 0.5- and 2-mm fractions. Although we could not ascertain this behaviour, some studies have demonstrated that particle size influences soil chemical composition and proffers different stability to microbial decomposition and thus different influence on P sorption stability (Sharpley et al., 1994). There is evidence to suggest that the particle size of plant residues has an influence on the amount of C stabilized in the soil during residue decomposition (Angers & Recous, 1997), particularly for organic residues with high amounts of N such as compost. In smaller particles (<1 mm), their C rapidly get stabilized in the very early stages of decomposition, resulting in the intimate contact between decomposing residues and soil mineral particles (Angers & Recous, 1997; Jensen, 1994). In the short term, the decomposition products of OM will become less available to compete for sorption sites with P, hence a temporary increase in P sorption. This phenomenon is only temporary as the decomposition process proceeds in the long term, resulting in OM decomposition products occupying sorption sites previously occupied by P, hence an increase in P in the soil solution.

3.3 | P sorption as a function of solution pH and particle size

P sorption under the different amendments is strongly dependent on solution pH (p < 0.001) (refer to Table 1 in Supporting Information). P sorption across all the amendments was very high at pH 4.5 ranging from 79.25 to 940.89 mg P kg⁻¹ across treatments and particle sizes and markedly decreased as pH increased, reaching the lowest (55.21–905.21 mg P kg⁻¹) at pH 7.5 (neutral) also across the different treatments and particle sizes (Figure 2). This was, however, more apparent at particle sizes of 2 and 0.5 mm, between added P concentrations of 50 and 100 ppm (Figure 2d-i). There was an interaction between pH and particle size on P sorption (refer to Table 1 in Supporting Information). Caporale et al. (2013) reported similar findings on the adsorption of arsenate by Al-WTR. Arsenate (AsO_4^{3-}) and phosphate (PO_4^{3-}) exhibit similar chemical properties (Bodek et al., 1988). P sorption is generally known to decrease with increasing pH (Goldberg & Sposito, 1984; Haynes, 1982). This is because high pH promotes variable negative charges that prevent clay particles in soils from absorbing phosphate ions (Barrow, 2017; Jin et al., 2005; Zeng et al., 2004). Some studies have also demonstrated mechanisms in which pH impacts P sorption. These include change of P forms in soil, exchange of ions and competition with other anions for adsorption sites (Bai et al., 2017; Zhou et al., 2005). At pH > 7,

phosphate ions compete for adsorption sites with hydroxyl (OH–) ions, resulting in low P sorption (Liu et al., 2011). Positive charges become abundant at low pH, which enhances P adsorption. For example, when pH is low, Al and Fe oxides become highly soluble, resulting in a greater propensity of soils containing these oxides for P sorption (Gérard, 2016; Gustafsson et al., 2012). These results support the need for liming soils to enhance the availability of P for plant uptake.

P sorption by the different amendments generally decreased in the order 0.25 mm > 0.5 mm > 2 mm, regarding the particle size of the amendments (Figure 2). Coarser fractions quickly reached P saturation as the adsorption curves flattened prematurely compared to 0.25- and 0.5-mm particle sizes (Figure 2). At 0.25-mm particle size, all four amendments exhibited a higher affinity for P as shown by a steeper curve compared to the 2- and 0.5-mm particle sizes. This could be a result of the grinding process, which probably exposed new mineral surfaces that would not be normally available for P adsorption. The decrease in particle size also creates a greater surface area for P adsorption by finer particles (Atalay, 2001; Leader et al., 2008; Xu et al., 2006). Andrieux-Loyer and Aminot (2001) also reported significant correlations between higher Al- and Fe-bound P and the finer soil fractions. Consideration of Al-WTR particle size is, therefore, important for applications where the intention is to reduce P sorption. Finer particles would suit soil remediation purposes, for example, in instances where there is excess P or heavy metal contamination in the environment. Although it should be noted that there is no published information on the changes in particle size of WTR when added to soil in field applications. Although the 0.25-mm particle size for compost showed higher P sorption, we assume this would not be a serious challenge as this immobilization should be only temporary as explained before and given that most compost used by farmers consists of particle sizes >0.25 mm.

The percentage of adsorbed P (adsorbed P to added P) decreased with increasing P concentration across all treatments (Figure 3). The percentage of adsorbed P also decreased with increasing pH, while it increased with a decrease in particle size (Figure 3). There was an increase in the relative P sorption between 10 and 50 mg PL^{-1} . After 50 mg L^{-1} , the relative P sorption decreased (Figure 3). Wang and Liang (2014) and Bai et al. (2017) reported similar trends from the investigation of phosphate adsorption and desorption in soils. P adsorption is regarded as a multistage process that is characterized by an initial rapid stage that eventually slows as the reaction proceeds (Wang & Liang, 2014). The P adsorption process can be divided into two phases-the chemical and the physical adsorption processes (Addiscott & Thomas, 2000; Lopez, 1996; Yang et al., 2019). The chemical adsorption phase precedes the physical phase and happens at low P concentrations. It is a rapid process that slows down at high P concentration as adsorption sites become saturated. It is presumed that ion and ligand exchange is the dominant mechanisms contributing to the rapid rate of adsorption in the chemical phase (Lai & Lam 2009). At this instant, phosphates are thought to react with amorphous Fe, Al and base cations in clay particles. The physical process is slower and is dominant at higher P

100

80

60

40

20

0

120

100

80

60

40

20

0

100

80

60

40

20

0

0

50

Relative P sorption (%)

(a)

(d)



FIGURE 3 Relative phosphorus (P) sorption (sorbed P/added P) for the different soil amendments (%). Error bars denote the least significant differences (LSDs) of the treatment means at p < 0.05 (N = 3). AI-WTR, aluminium water treatment residual; C, compost.

concentrations (Lai & Lam 2009; Lopez et al., 1996). In the physical process, P sorption through the chemical process reaches a state of saturation, hence the P present in equilibrium solution can only be adsorbed through physicochemical and physical adsorption (through weak intermolecular forces) with the soil. In the physical process, the adsorbed P is more strongly retained in the soil, forming nonlabile P (Quintero et al., 1999). The slow physical process happens over a longer period and can take several years (Barrow, 2015).

3.4 P adsorption equations

Several models have been put forward to describe P adsorption isotherms. The Langmuir and Freundlich adsorption isotherms are the most popular ones (Yang et al., 2019). P sorption was well described by the Langmuir isotherm, with coefficients of determination (R^2) ranging between 0.66 and 0.99 across all the treatments (Table 2).

This indicated a better fit compared to the Freundlich isotherm, where R^2 varied from 0.22 to 0.88 (Table 2). Results from other related studies (Bai et al., 2014; Caporale et al., 2013; Yang et al., 2019) are consistent with our findings. Therefore, the P adsorption parameters that include the P maximum adsorption capacity (Q_0) , the bonding energy constant (b) and the MBC were calculated from the Langmuir isotherm. These parameters are generally used to determine the availability of P in soil and the related P adsorption capacity (Yang et al., 2019). In addition, the PFRs due to the different amendments were also calculated based on the Langmuir isotherm.

Langmuir adsorption parameters 3.5

The P sorption parameters estimated from the Langmuir equation varied significantly among the treatments. The maximum P

200

250

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pН	Particle size (mm)	R ² Langmuir	R ² Freundlich	Q_0 (mg kg ⁻¹)	<i>b</i> (L mg ⁻¹)	MBC (L kg ⁻¹)	EPR (0.2) (mg kg ⁻¹)	P ₂ O ₅ (mg kg ⁻¹)	P₂O₅ (kg ha ^{−1})
5% C	C + 5% AI-WTR								
4.5	2	0.9712	0.7686	769.23	0.06	48.54	11.59	26.55	53.10
	0.5	0.9813	0.6990	769.23	0.09	70.42	15.83	36.26	72.52
	0.25	0.9990	0.4991	909.09	0.39	357.14	68.26	156.31	312.63
6.5	2	0.9587	0.7764	625.00	0.08	49.01	11.65	26.67	53.35
	0.5	0.9839	0.7397	714.29	0.09	65.36	14.84	34.00	67.97
	0.25	0.9986	0.6014	833.33	0.32	270.27	52.80	120.92	241.84
7.5	2	0.9844	0.7848	555.56	0.10	54.05	12.60	28.85	57.70
	0.5	0.9752	0.7539	714.29	0.07	52.08	12.27	28.10	56.21
	0.25	0.9930	0.6423	769.23	0.32	243.90	47.85	109.57	219.13
10%	C + 10% AI-WTR								
4.5	2	0.9917	0.6334	833.33	0.32	113.63	24.11	55.21	110.41
	0.5	0.9960	0.5688	833.33	0.32	263.16	51.47	117.86	235.72
	0.25	0.9940	0.4393	1000.00	0.45	588.23	109.93	251.74	503.49
6.5	2	0.9975	0.6560	714.29	0.32	156.25	31.93	73.13	146.25
	0.5	0.9937	0.5981	769.23	0.41	312.50	59.76	136.86	273.72
	0.25	0.9995	0.4641	909.09	0.61	500.00	91.13	208.68	417.36
7.5	2	0.9967	0.6883	714.29	0.22	121.95	25.59	58.60	117.19
	0.5	0.9930	0.6340	769.23	0.28	212.77	43.20	96.86	193.72
	0.25	0.9952	0.5041	909.09	0.76	454.55	80.91	185.30	370.59
10%	С								
4.5	2	0.6696	0.8528	476.19	0.02	9.28	3.85	8.81	17.63
	0.5	0.8486	0.7461	434.78	0.03	14.75	4.93	11.30	22.59
	0.25	0.9623	0.8130	909.09	0.07	62.11	14.25	32.63	65.27
6.5	2	0.9352	0.8475	243.90	0.04	10.95	4.17	9.56	19.11
	0.5	0.8573	0.8100	357.15	0.03	11.93	4.37	10.01	20.02
	0.25	0.9576	0.8476	769.23	0.06	44.44	10.78	24.69	49.38
7.5	2	0.9239	0.8685	243.90	0.04	9.69	3.92	8.98	17.97
	0.5	0.9712	0.7833	294.12	0.04	12.47	4.47	10.25	20.49
	0.25	0.9992	0.8699	769.23	0.05	35.21	8.97	20.55	41.09
10%	AI-WTR								
4.5	2	0.9977	0.4797	833.33	0.32	270.27	51.47	117.86	235.72
	0.5	0.9995	0.4460	909.09	0.55	500.00	92.09	210.89	421.77
	0.25	0.9993	0.2382	1000.00	0.91	909.09	171.20	392.06	784.12
6.5	2	0.9980	0.6125	769.23	0.32	243.90	47.85	109.57	219.13
	0.5	0.9988	0.5258	909.09	0.44	400.00	75.53	172.96	345.92
	0.25	0.9997	0.2229	909.09	1	909.09	153.52	351.55	703.10
7.5	2	0.9967	0.6467	769.23	0.23	175.43	35.54	81.39	162.79

TABLE 2 Parameters of phosphorus adsorption characteristics and external phosphorus fertilizer requirements as described by the Langmuir equation.

TABLE 2 (Continued)

pН	Particle size (mm)	R ² Langmuir	R ² Freundlich	Q ₀ (mg kg ⁻¹)	<i>b</i> (L mg ⁻¹)	MBC (L kg ⁻¹)	EPR (0.2) (mg kg ⁻¹)	P₂O₅ (mg kg ^{−1})	P₂O₅ (kg ha ^{−1})
	0.5	0.9987	0.5590	833.33	0.39	322.58	61.85	141.63	283.26
	0.25	0.9992	0.3062	909.09	1.00	909.09	153.52	351.55	703.10

Abbreviations: *b*, a constant related to the binding strength of P at the adsorption sites ($L mg^{-1} P$); EPR_{0.2}, external P fertilizer requirement based on 0.2 mg P L⁻¹ in soil solution (mg kg⁻¹); MBC, maximum buffering capacity (L kg⁻¹); Q₀, maximum P adsorption capacity (mg P kg⁻¹).

adsorption capacity, (Q_0) , which has been widely used to estimate the P adsorption capacity of a soil (Yan et al., 2013), decreased with an increase in pH across treatments and generally also decreased as particle sizes increased (Table 2). Xu et al. (2006) also reported a positive correlation between the P sorption maximum and the finer soil fractions (<0.5-mm particle sizes). This underscores the important role of particle size in the retention of added P, which can have a bearing on AI-WTR disposal or its use in agriculture in the long term. Across treatments, the P adsorption maxima decreased in the order 10% AI-WTR > 10% coamendment > 5% coamendment > 10% C (p < 0.01). As a soil reaches its maximum sorption capacity, it is less able to sorb P, leading to increased soil solution P, but also increasing the risk of P loss by runoff or leaching (Kleinman, 2017). At an amendment rate of 10% AI-WTR, P would be rendered unavailable to plants due to its high maximum P sorption, while soils amended with 10% C would require best management practices to prevent P loss by leaching due to a low Q_0 . Based on our results, it would be best to amend soils at 5% coamendment, which has a more moderate P sorption maxima than both 10% coamendment and 10% Al-WTR, leaving more P available for plant requirements. Q_o also reflects the relative number of P adsorption sites per unit of soil weight. A higher Q_{0} automatically means a higher number of sites available for P adsorption. Results point to a higher number of adsorption sites in 10% Al-WTR, which we correlated with the higher amount of Al relative to the other treatments, while 10% C has fewer adsorption sites for P sorption due to high OM content, which competes for adsorption sites. Some studies have demonstrated correlations between Q₀ and SOM contents or Fe and Al (Villapando & Graetz, 2001; Zhang et al., 2005).

The P bonding energy constant, *b*, is another important parameter, which is used to describe the affinity of soil for P. A higher constant value, *b*, as in 10% Al-WTR (Table 2) indicates higher strength in P adsorption. Spontaneous P adsorption will occur readily as soil solution P declines (Wang & Liang, 2014). Ten percent of C with the lowest *b* values has the least affinity for P. However, 5% coamendment had a lower value for *b* compared to 10% Al-WTR and 10% coamendment, indicating its lower strength in sorbing P, despite equal ratios of Al-WTR and compost. The results show that the bonding energy constant increase in adsorption sites. The bonding energy constant, like the P adsorption maximum capacity, generally increased as particle size became finer as well with a decrease in solution pH, although there were a few exceptions that were

inconsistent, for example, in 5% coamendment (Table 2). We could only relate that to a possible precipitation of P by calcium ions, as the pH increased.

MBC was highest in 10% Al-WTR and least in 10% C (Table 2). MBC refers to the measure of the capacity of soil to resist a change in its P concentration as P is removed by plant uptake or added to fertilizer or organic materials (Holford, 1997). The MBC numerical value is a product of Q_0 and b in the Langmuir equation. Soil factors that influence Q_0 and b directly influence the MBC. Consequently, MBC also increased with a decrease in particle size and was generally higher at low pH across the different treatments (Table 2). A higher MBC value indicates a higher P adsorption capacity and vice versa. A higher MBC would also point to a higher PFR (Table 2). Using this concept, results showed that a soil amended with 10% Al-WTR would adsorb more P as compared to the other amendments (see Figure 2). Consequently, soils amended with AI-WTR would require high inorganic fertilizer P rates to maintain a desired P concentration in the soil solution for good plant growth. This was apparent in the higher PFRs (Table 2). For example, the highest PFR for a soil amended with 10% AI-WTR was 774.12 kg P₂O₅ ha⁻¹ (pH 4.5; 0.25mm particle size) compared to $503.49 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$ (10% coamendment), 312.63 kg P_2O_5 ha⁻¹ (5% coamendment) and 65.27 kg P_2O_5 ha⁻¹ (10% C) at similar pH and particle size (Table 2). As discussed, the higher amount of exchangeable AI in the AI-WTR would have resulted in the high P sorption and consequently a higher amount of P fertilizer required to satisfy the P adsorption sites and maintain optimal P concentration in the soil solution for good plant growth. However, the 10% and 5% coamendments showed an apparent reduction in PFRs by ranges of 30%-60% and 60%-70%, respectively, across the different pH and particle sizes relative to 10% Al-WTR (Table 2). In our previous work (Gwandu et al., 2021), the application of 14 kg P ha⁻¹, which translates to 32 kg P_2O_5 ha⁻¹ was far below the minimum of 57 and 117 kg P_2O_5 ha⁻¹ estimated at a pH of 7.5- and 2-mm particle size for the 5% and 10% coamendment, respectively (Table 2). The ability of an organic material to reduce or increase P sorption is dependent upon its type, its P concentration and the amount added (Singh & Jones, 1976). Organic materials containing 0.3% P or more result in a decrease in P sorption, while those with less than 0.22% increase P sorption (Singh & Jones, 1976). The compost used in this study had 0.18% P (see Table 1). While our results show about 5 times as much PFR for the 5% coamendment compared to 10% C, a good quality compost (>0.3% P) can result in increased P availability and thus less PFRs.

We, therefore, recommend the determination of P levels of organic amendments before a decision can be made to coapply with Al-WTR.

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4 | ENVIRONMENTAL AND AGRICULTURAL IMPLICATIONS FOR THE USE OF AL-WTR IN SOIL HEALTH IMPROVEMENT

Our experimental results confirmed that the maximum P adsorption increased with a decrease in particle size and pH. This has potential implications for the disposal of Al-WTR in the environment or its use as a soil applicant. Although research has provided evidence of the soil health benefits of coamending AI-WTR and compost (Gwandu et al., 2021; Hsu & Hseu, 2011; Kerr et al., 2022; Mahmood-ul-Hassan et al., 1993), consideration of Al-WTR particle size is therefore important to reduce P sorption and increase P availability in coamended soils. Finer particles would suit soil remediation purposes such as in instances where there is excess P or heavy metal contamination in the environment. Although in real circumstances, field applications of Al-WTR will not involve grinding into finer particles, we presume the Al-WTR will break down into smaller particles due to mechanical weathering and decomposition processes, resulting in a larger surface area, and potentially exposing new P adsorption sites. Further studies to determine the rate of breakdown of AI-WTR in sandy soils might be required to come up with recommendations on P fertilization strategies. Meanwhile, to maintain yield stability, integrated use of Al-WTR, OM and P fertilizer is recommended. Apart from stabilizing plant yields, the combined use of organic materials and P fertilizers is an important component of integrated soil fertility management. This has also been proven to reduce greenhouse gas emissions from soils and fertilizers (Bayu, 2020), which is beneficial for human health.

5 | CONCLUSIONS

P sorption onto Al-WTR is best represented by the Langmuir adsorption isotherm. The maximum P sorption capacity was in the ranges of 217–769, 555–909, 714–909 and 769–1000 mg kg⁻¹ for 10% C, 5% coamendment, 10% coamendment and 10% Al-WTR, respectively, across the various particle fractions and pH. The crop PFRs, based on a minimum of 0.2 mg P L⁻¹ in solution ranged from the lowest of 53 kg P₂O₅ ha⁻¹ in 10% C (pH 7.5; 2 mm particle size) to the highest of 784 kg P₂O₅ ha⁻¹ in 10% Al-WTR (pH 4.5; 0.25-mm particle size). Results also revealed that 10% and 5% coamendments reduced the P fertilizer required to maintain a minimum of 0.2 mg P L⁻¹ by ranges of 30%–60% and 60%–70%, respectively, relative to 10% Al-WTR. The results indicate that coamending Al-WTR and compost can increase P availability in Al-WTR amended soils, providing scope for use of Al-WTR in rebuilding soil health. Detailed analysis of factors such as particle size, soil pH and P concentration

levels of the organic amendments, which can maintain and enhance P availability in coamended sandy soils, can be further exploited to inform long-term use of Al-WTR in rebuilding soil health and boost food production to support human health.

AUTHOR CONTRIBUTIONS

Tariro Gwandu: Conceptualization; methodology; formal analysis; investigation; writing-original draft; writing-review and editing. Noxolo S. Lukashe: Methodology; writing-review and editing. Jairos Rurinda: Writing-review and editing. Wendy Stone: Writing-review and editing. Stephen Chivasa: Writing-review and editing; supervision. Catherine E. Clarke: Methodology; writingreview and editing; administration. Hatirarami Nezomba: Writingreview and editing. Florence Mtambanengwe: Writing-review and editing; visualization; project administration; supervision. Paul Mapfumo: Writing-review and editing. Jan G. Steytler: Writing-review and editing. Karen L. Johnson: Conceptualization; methodology; writing-review and editing; visualization; supervision; project administration; funding acquisition.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available within the article [and/or] its Supporting Information: Material.

ETHICS STATEMENT

The authors declare that they adhered to the ethical policies of the *Journal of Sustainable Agriculture and Environment* as described in the "Best Practice Guidelines on Research Integrity and Publishing Ethics" document.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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